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METHODOLOGY FOR ASSIGNMENT OF A HYDROCARBON PHOTOCHEMICAL REACTIVITY INDEX FOR EMISSIONS FROM MOBILE SOURCES

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National Environmental Research Center
Research Triangle Park, North Carolina

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An analytical scheme is presented which permits assessment of the photochemical significance of light-duty mobile source hydrocarbon emissions. The scheme incorporates both the mass and atmospheric reactivity of the hydrocarbon emissions. Analytical procedures supplementary to those defined for light-duty mobile source certification in the Federal Register are defined. The analytical procedures permit definition of four basic reactivity classes of hydrocarbons: Class I, nonreactive, including methane, ethane, acetylene, propane, and benzene; Class II, reactive, including the C_4 and higher paraffins; Class III, reactive, including the aromatics except benzene; and Class IV, reactive, including the olefins. Procedures for assignment of a Hydrocarbon Photochemical Reactivity Index utilizing the reactivity definition in conjunction with the mass of emissions are described in detail.

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METHODOLOGY FOR ASSIGNMENT OF A HYDROCARBON PHOTOCHEMICAL REACTIVITY INDEX FOR EMISSIONS FROM MOBILE SOURCES

INTRODUCTION

Air quality criteria for photochemical oxidants have been established in accordance with Section 107(6) of the Clean Air Act (42 U.S.C. 1857-18571).[1] The current approach to abatement of photochemical oxidants is based on control of organic emissions. Mobile source certification procedures dictate control of total hydrocarbon emissions. Many studies have been reported[2-5] that indicate that organic emissions participate in atmospheric reactions leading to oxidant/ozone formation in varying degrees. The consensus of these studies indicates that methane, ethane, acetylene, propane, and benzene, under reasonable hydrocarbon-to-NO_x ratios, are essentially nonreactive.

Since the standard requiring hydrocarbon emission control is based on oxidant/ozone formation, procedures for measurement of both mass and reactivity of hydrocarbon emissions are necessary to evaluate adequately the potential impact on photochemical pollution of prototype hydrocarbon control systems.

Current research practices entail detailed analysis of more than 50 hydrocarbon compounds commonly found in exhaust samples. These are weighted by reactivity. The chromatographic procedures required for the analysis of the individual hydrocarbons are cumbersome and beyond the capabilities of many interested laboratories. It is the intent of this report to suggest less cumbersome procedures that will permit assignment of a Hydrocarbon Photochemical Reactivity Index for mobile sources.

Hydrocarbon reactivity has been utilized as an index of participation in atmospheric reactions leading to oxidant/ozone formation. Within the context of this report, hydrocarbons will be addressed in four basic reactivity classes as set forth in Table 1.

Table 1. REACTIVITY CLASSIFICATION OF MOBILE SOURCE HYDROCARBON EMISSIONS[5]

Class	Compounds	Molar reactivity rating
I (nonreactive)	Methane, ethane, acetylene, propane, benzene	1.0
II (reactive)	C_4 and higher paraffins	6.5
III (reactive)	Aromatics less benzene	9.7
IV (reactive)	Olefins	14.3

A newly developed gas chromatographic procedure for measurement of the nonreactive hydrocarbons, Class I, will be discussed in detail. Further, the integration of this procedure with previously described subtractive techniques[6] will be discussed for measurement of the three reactive classes.

EXPERIMENTAL

NONREACTIVE HYDROCARBON MEASUREMENT

A gas chromatographic system has been developed that will permit quantitative analysis of methane, ethane, acetylene, propane, and benzene. The system, which includes four packed columns operated in a Perkin-Elmer Model 900 gas chromatograph (GC) equipped with a flame ionization detector, is basically illustrated in Figure 1. Multiple columns are required because of the significantly different physical and chemical character of the compounds being determined and because of the large variety of potentially interfering compounds found in normal samples. The interfering compounds include a wide range of other hydrocarbons, oxygenates, sulfur- and nitrogen-containing organics, and the inorganics O_2, N_2, CO_2, CO, NO, and NO_2. The described column system permits baseline resolution of the five hydrocarbons defined as nonreactive.

The method involves injection of two sample aliquots: The first on columns 1 and 2 for methane, ethane, acetylene, and propane analysis; and the second on columns 3 and 4 for benzene analysis. Both aliquots are directed to a single detector, with columns 1 and 2 being backflushed to vent during the period when benzene is eluting from columns 3 and 4. The second aliquot is injected so as to permit elution of the C_3 hydrocarbons of interest prior to elution of the benzene.

The details of the system are illustrated in Figure 2. Column 1, which consists of 96- by 1/8-inch o.d. stainless steel tube packed with 80/100-mesh Poropak Q, is used primarily to resolve methane from air. Normally, air is considered not to produce a signal of significance in a flame ionization detector. However, when the detector/signal amplifier

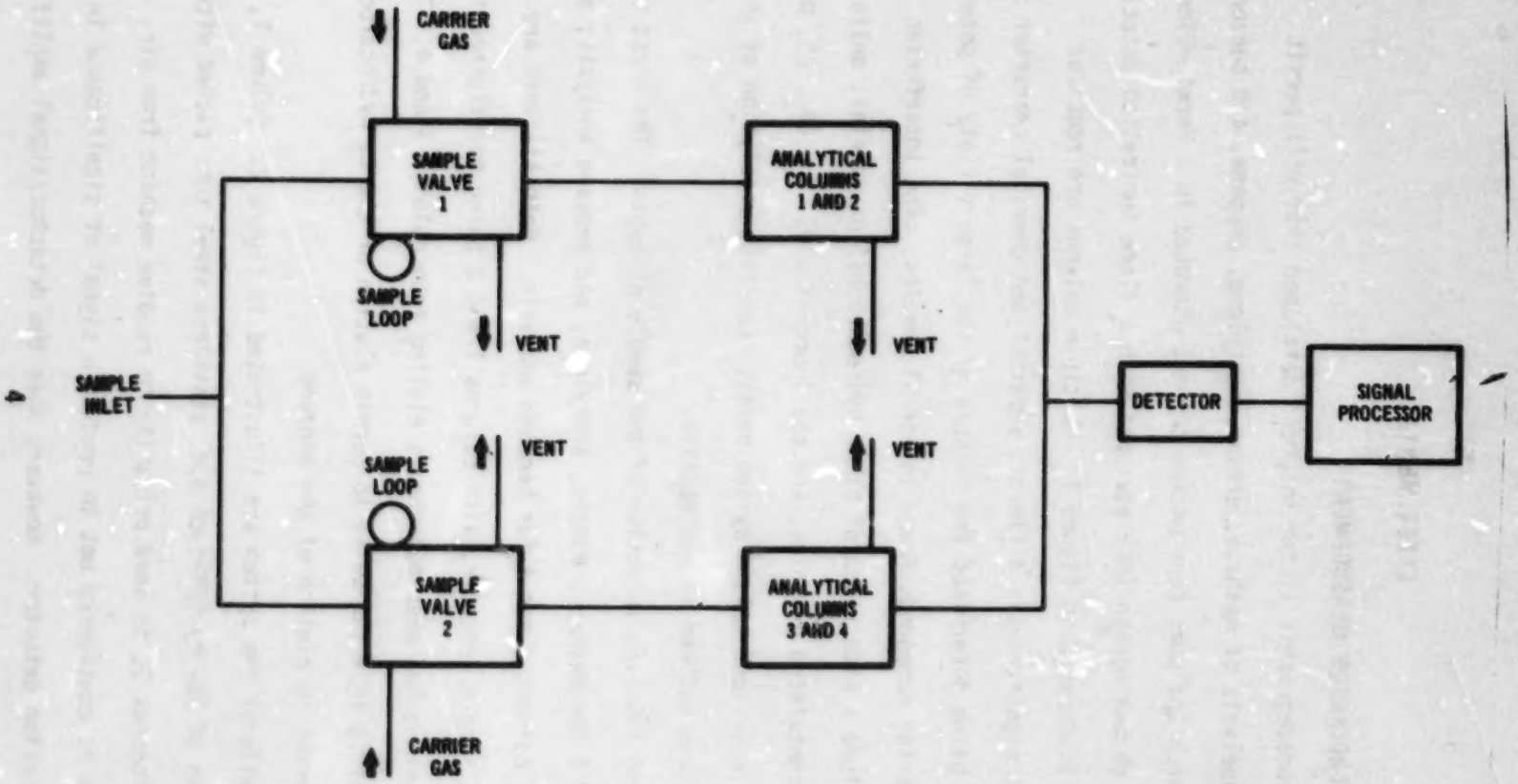

Figure 1. Gas chromatographic system block diagram.

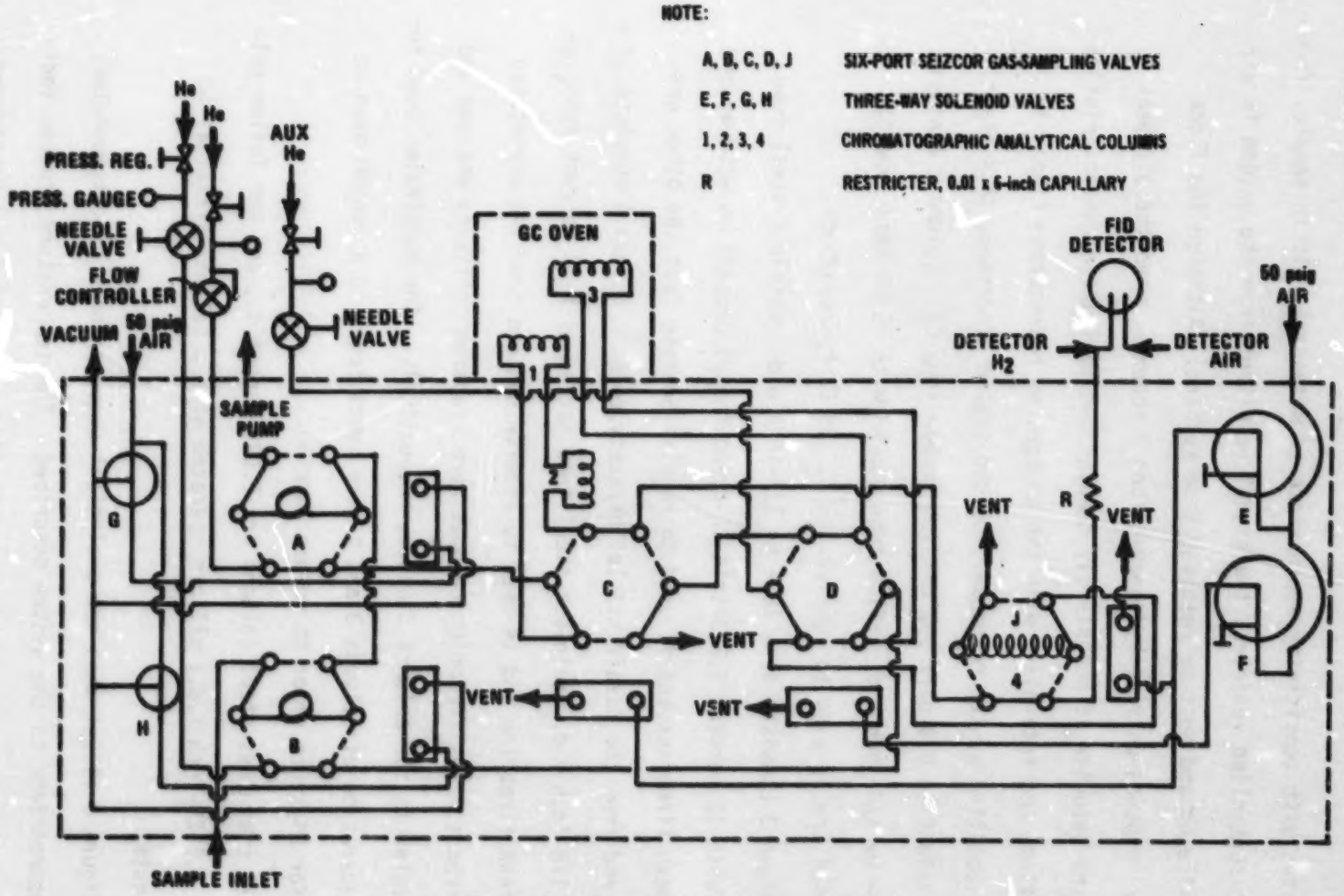

Figure 2. Chromatographic flow scheme.

is operated with sensitivity appropriate to methane levels in samples from emission-controlled vehicles, the signal resultant from the oxygen in air is significant and must be resolved from methane. Although the flame detector responds only to hydrogen-carbon compounds, when the air peak enters the detector it momentarily changes the ionization characteristics of the flame and interplays with the background hydrocarbon signal to yield a positive system response. On the system described, this signal is equivalent to 0.9 part per million carbon (ppm C). Column 2 consists of a 48- by 1/8-inch o.d. Teflon tube packed with 35/60-mesh Type 58 Silica Gel and is used to resolve the C_2 and C_3 hydrocarbons.[7]

Column 3 consists of a 180- by 1/8-inch o.d. stainless steel tube packed with 15 percent 1,2,3-tris (2-cyanoethoxy) propane on acid-washed 60/80-mesh firebrick and is used to resolve benzene from the other aromatics and from the paraffins/olefins/acetylenes.[8] Column 4 consists of a 24- by 1/8-inch o.d. stainless steel tube packed with 20 percent $HgSO_4$ on 30/40-mesh firebrick and is used to resolve benzene from the oxygenated hydrocarbons. The firebrick columns were prepared utilizing acetone and water solvents for columns 3 and 4, respectively. The substrates used for the preparation of columns 3 and 4 were conditioned in a vacuum oven at 110°C for 24 hours prior to column packing.

The stainless steel columns are 0.093-inch i.d., and the Teflon column is 0.0625-inch i.d.; all are operated with a helium carrier at 50 cm^3/minute.

Figure 3 illustrates the analytical sequence on a time-temperature plot appropriate to the system described. The temperature program indicated applies only to columns 1 and 3. Columns 2 and 4 are maintained

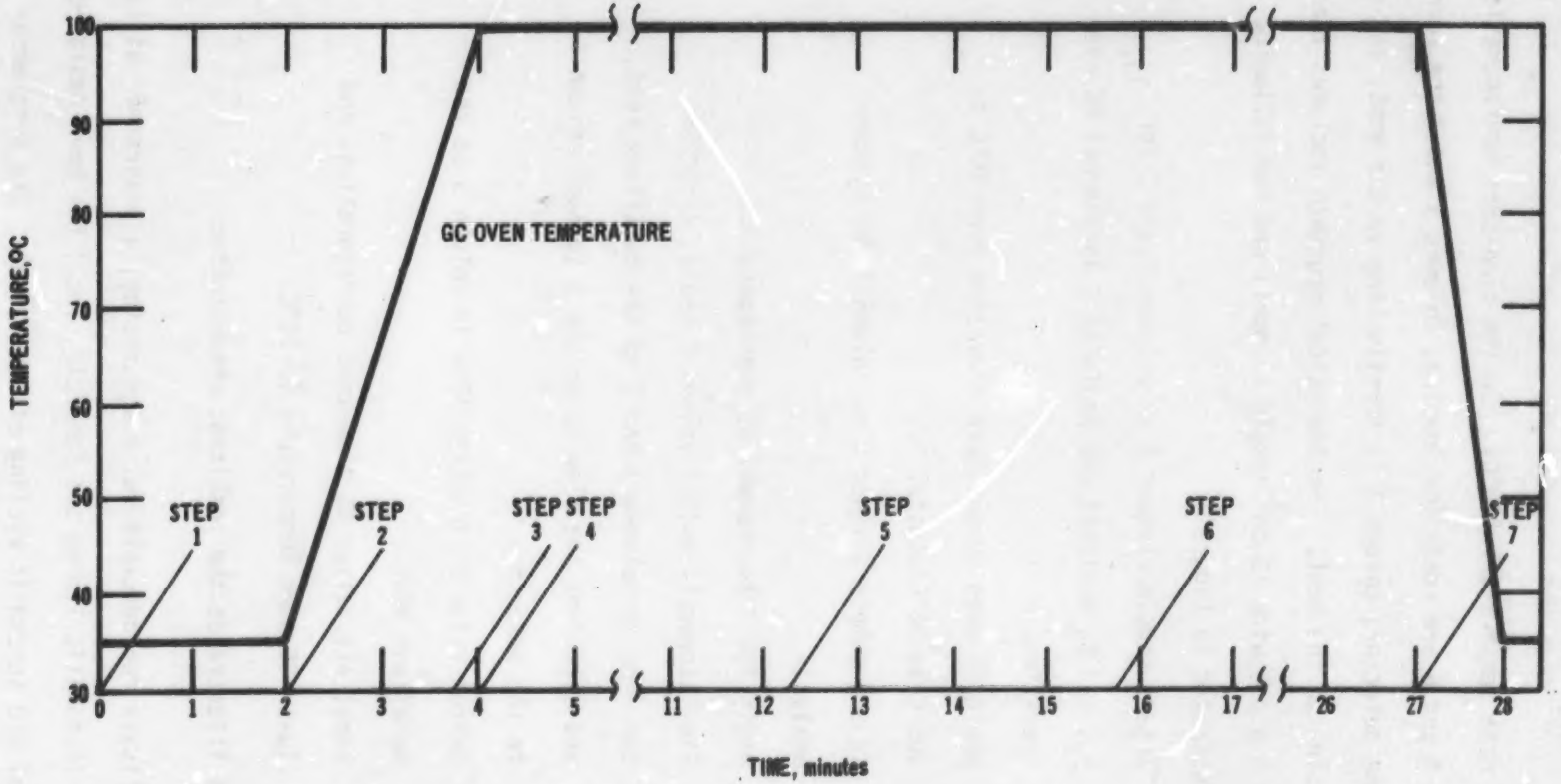

Figure 3. System operation sequence.

isothermal at room temperature (20°C). In the time-zero configuration, sample valves A and B are ready for loading, columns 1 and 2 are foreflushing to the detector, column 3 is foreflushing to the vent, and column 4 is backflushing to the vent. The analytical sequence includes loading sample valves A and B with 10-cm^3 sample aliquots and the following steps, as illustrated in Figure 3:

Step 1. Inject sample aliquot A on columns 1 and 2 for C_1, C_2, and C_3 analysis and begin 35°C isothermal GC oven operation.

Step 2. Begin GC oven temperature elevation from 35°C to 100°C at 32°C/minute.

Step 3. Inject sample aliquot B on column 3 for benzene analysis.

Step 4. Begin 100°C isothermal GC oven operation.

Step 5. Simultaneously switch valves C and J, directing the flow in columns 1 and 2 to the backflush vent, and directing the flow in column 3 through column 4 to the detector.

Step 6. Switch valve D directing flow in column 3 to the backflush vent.

Step 7. Reset all valves to time-zero configuration, and lower GC oven temperature to 35°C.

Figure 4 illustrates the resultant chromatogram.

To facilitate reproducible valve sequencing, a programmer utilizing three timers (Automatic Timing and Controls, Inc.) has been designed that permits manual and automatic cycling of the valves. The programmer is

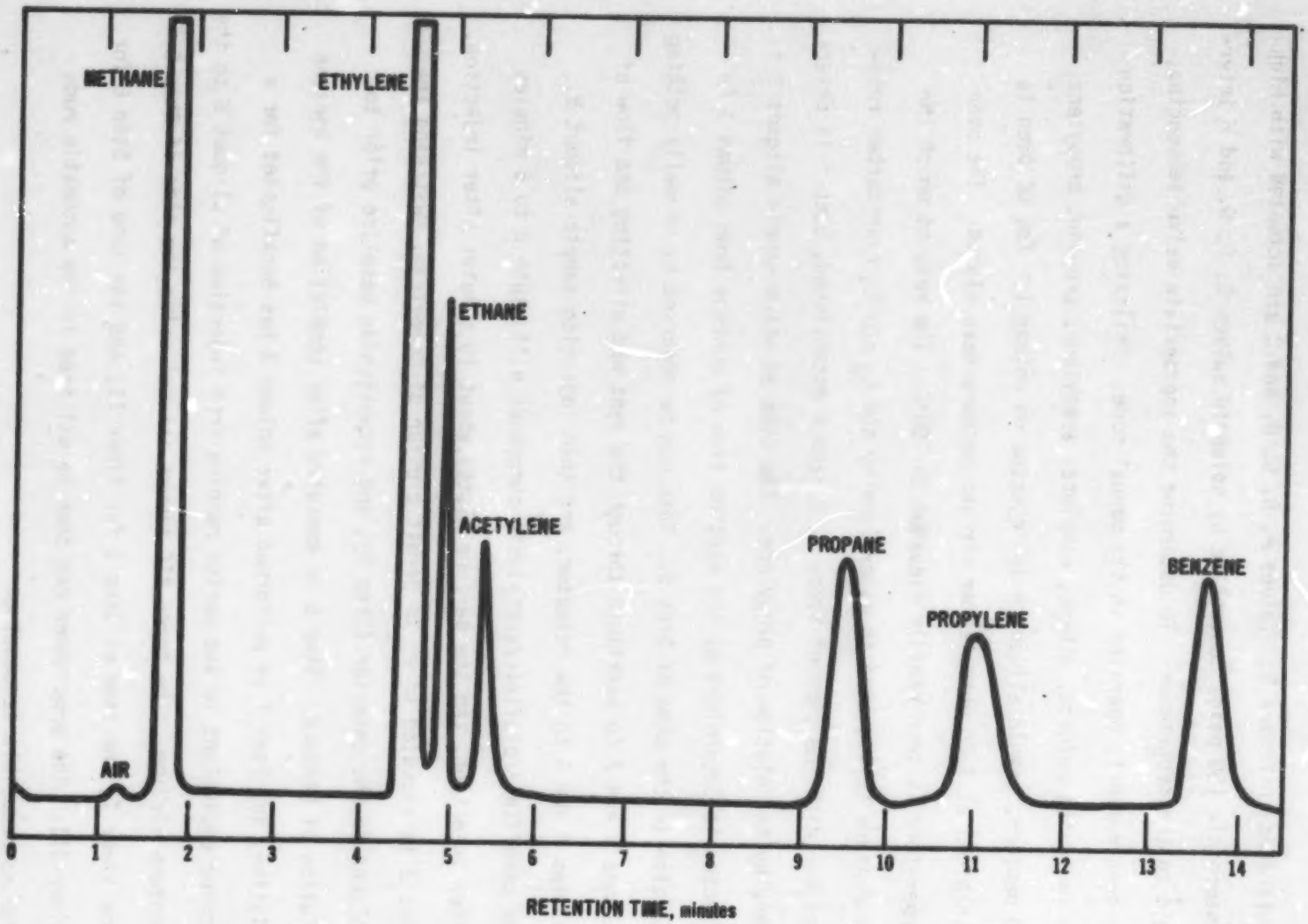

Figure 4. Chromatogram of calibration mix.

illustrated in Figure 5. Valves A, B, C, D, and J are actuated with high-pressure air (50 psig) controlled by solenoid valves E, F, G, and H interfaced to the programmer. To determine the appropriate valve sequencing, the programmer is operated in the manual mode. Utilizing a calibration mix including methane, ethane, ethylene, acetylene, propane, propylene, and benzene, sample aliquot A is injected on column 1. The GC oven is maintained at 35°C until after air and methane have eluted. The oven temperature is then rapidly elevated to 100°C. The rate at which the temperature is elevated is determined by the C_2 and C_3 hydrocarbon resolution. With the time of Steps 1, 2, and 4 established, Step 5 is determined by the elution of propylene. The time at which sample aliquot B is injected is determined by the elution time of benzene from column 3 in relation to the time of Step 5. This can be observed by manually setting columns 1 and 2 to backflush through the vent and directing the flow of columns 3 and 4 to the detector, and then injecting sample aliquot B. The paraffinic/olefinic/acetylenic compounds will elute 2 to 6 minutes after injection, and the benzene elutes about 10 minutes after injection. Step 3 is executed so as to permit elution of propylene, switching the columns to the detector (Step 5), and establishing baseline prior to elution of benzene. Step 6 is executed after completion of the benzene elution, and Step 7 is performed after column 3 has backflushed for a period equivalent to the period running from injection of aliquot B to the benzene elution. The three ATC timers are set using the time of Step 3 for timer I, the time of Step 5 for timer II, and the time of Step 6 for timer III. The programmer can then be utilized in the automatic mode for reproducible sequencing.

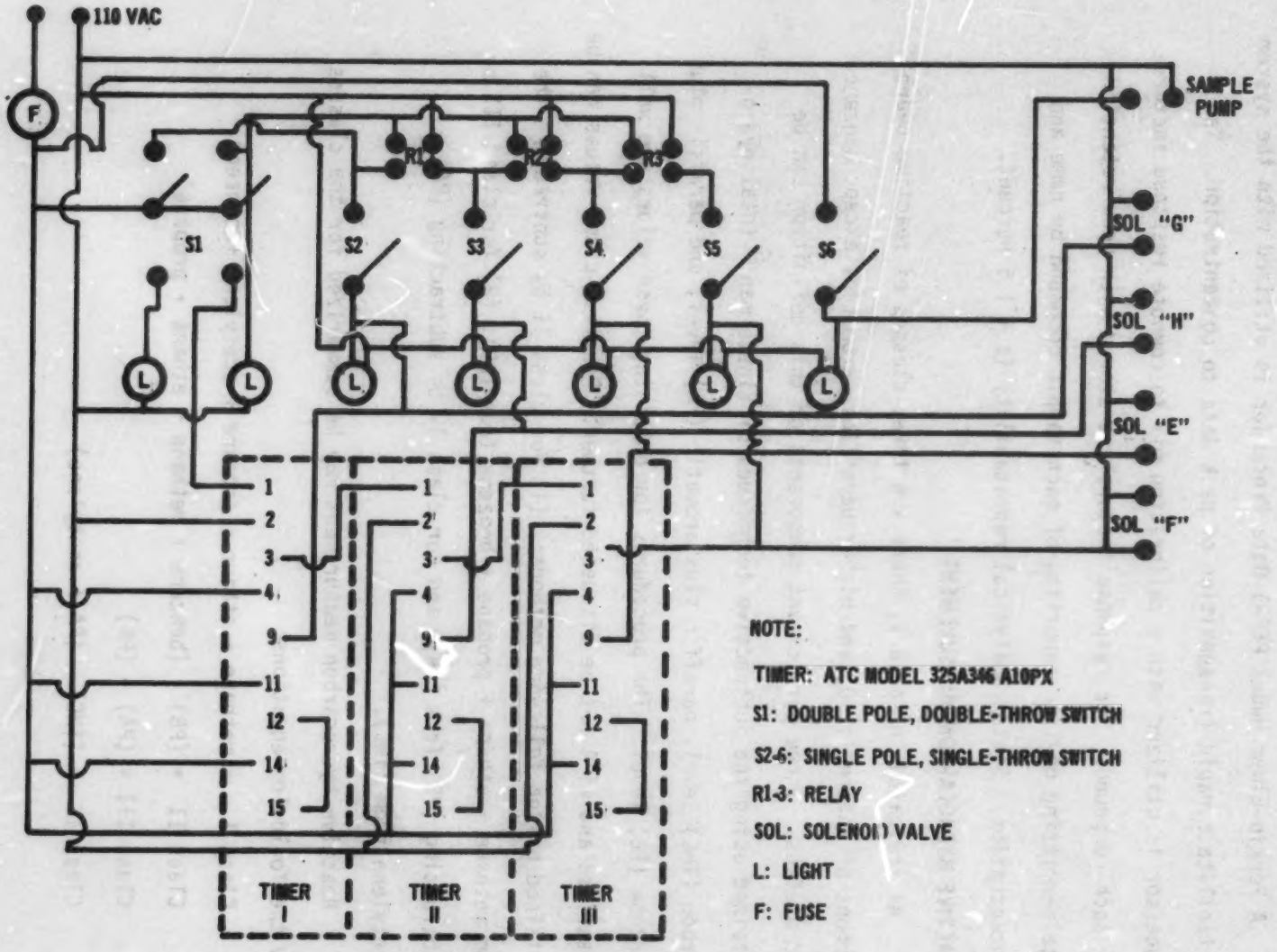

Figure 5. Valve programmer.

A Perkin-Elmer Model PEP-1 Data Processor is utilized with the system to facilitate rapid transposition of peak data to concentration. The processor is utilized with a calibration mix to compute response factors for each compound. The response factors are stored with peak retention data permitting on-line reporting of each sample compound by name and concentration. System analytical repeatability is $\pm$ 1.5 percent.

REACTIVE HYDROCARBON MEASUREMENT

As indicated in Table 1, there are three classes of reactive hydrocarbons of interest: C_4 and higher paraffins, aromatics except benzene, and olefins. Three participant components of this definition can be obtained using the subtractive techniques of Klosterman:[6] total hydrocarbon (THC) level, paraffin plus aromatic (PA) level, and paraffin plus benzene (PB) level. The procedures for obtaining these values are well described and will not be discussed further. Reactive class values can be obtained by the following methods: (1) for class II by subtracting the sum methane + ethane + propane + benzene from (PB); (2) for class III by subtracting (PB) from (PA); and for class IV by subtracting (PA) + acetylene from (THC).

Reactive hydrocarbon measurement may be summarized for the classes by the following equations:

Class I = methane + ethane + propane + acetylene + benzene

Class II = (PB) - (benzene + methane + ethane + propane)

Class III = (PA) - (PB)

Class IV = (THC) - (PA + acetylane)

RESULTS AND DISCUSSION

Currently defined procedures for certification of light-duty motor vehicles[9] call for collection of three exhaust samples: sample 1, "transient cold start" test-phase emissions; sample 2, "stabilized cold start" test-phase emissions; and sample 3, "transient hot start" test-phase emissions. These samples are collected with a Constant Volume Sampler, which dilutes the auto exhaust with air. Three dilution air samples are collected concurrent with the exhaust samples. There are thus six hydrocarbon analyses required per certification run--three samples and three backgrounds. These values are utilized to calculate the weighted mass emissions of hydrocarbons in grams per vehicle mile. The suggested procedure inserts reactivity in this calculation and results in a Hydrocarbon Photochemical Reactivity Index for the vehicle.

CALCULATIONS

The reactivity rating for each test-phase sample is calculated as follows:

$$R_{ht,s,ct} = \frac{(\%\ I \times r_1) + (\%\ II \times r_2) + (\%\ III \times r_3) + (\%\ IV \times r_4)}{100} \quad (5)$$

where:

R = reactivity rating value calculated for each test phase, i.e., cold transient, stabilized, and hot transient.

% I, II, III, IV = mass percentage of total hydrocarbon determined to be in classes I, II, III, and IV, respectively.

$$\% I = 100 \frac{\text{exhaust class I hydrocarbons, ppm C}}{\text{exhaust total hydrocarbons, ppm C}}$$

$r_{1,2,3,4}$ = mass reactivity rating for class I, II, III, and IV hydrocarbons.

A prerequisite for the determination of class mass reactivity ratings is definition of the average carbon number of the class emissions. The average carbon number can be used in conjunction with the molar reactivity ratings given in Table 1 to determine the mass reactivity ratings. Detailed hydrocarbon analysis is required to determine the class average carbon number. The procedures described generate a detailed analysis of class I, but not of classes II, III, and IV hydrocarbons. Tables 2 and 3 tabulate class average carbon numbers for several fuels and exhaust samples, respectively, as determined by detailed hydrocarbon analysis.

As can be seen, the average carbon number is dependent on fuel and on the combustion/control system. The sampling procedures (test cycle) will also affect the exhaust class average carbon number.

The reactivity ratings utilized by the author will be based on samples resultant from vehicles operated with the current Federal Test Procedure (three test phases) and a regular-grade unleaded fuel. The average carbon numbers utilized to determine the mass reactivity ratings are 5.55, 7.58, and 2.85 for classes II, III, and IV, respectively. Class I ratings are determined on a sample-by-sample basis as detailed information is available.

$$r_1 = \frac{1.0}{\text{average carbon number of test phase class I hydrocarbons}}$$

$$r_{2,3,4} = \frac{6.5}{5.5}, \frac{9.7}{7.58}, \frac{14.3}{2.58}$$

$$r_{2,3,4} = 1.2, 1.3, 5.0$$

Table 2. HYDROCARBON REACTIVITY CLASS AVERAGE CARBON NUMBERS, FUEL

Sample	Average carbon number, reactivity class			
	I	II	III	IV
Fuel (1) API-1 Premium leaded 1968	6.00	6.18	7.43	6.08
Fuel (2) API-8 Premium unleaded 1968	6.00	5.78	7.85	5.59
Fuel (3) API-10 Regular unleaded 1968	6.00	5.72	7.99	5.91
Fuel (4) Indolene Regular unleaded 1972	6.00	6.31	7.49	4.67
Fuel (5) Phillip's 66 EPA special Regular unleaded 1973	6.00	6.68	7.63	4.87

As specified in the Federal Register,[9] the mass emissions for each test phase are calculated as follows:

$$Y_{ht,s,ct} = V\ mix \times density\ HC \times \frac{HC\ conc}{10^6}$$

where:

Y = mass emissions in grams hydrocarbon per test phase

V mix = total dilute exhaust volume in cubic feet per test phase corrected to standard conditions (528°R and 760 mm Hg).

Table 3. HYDROCARBON REACTIVITY CLASS AVERAGE CARBON NUMBERS, EXHAUST

Sample	Test phase	Average carbon number, reactivity class			
		I	II	III	IV
1968 vehicle 1969 Federal Test Procedure Fuel (1)		1.58	6.35	7.55	3.16
1968 vehicle 1969 Federal Test Procedure Fuel (2)		1.77	5.97	7.98	3.54
1968 vehicle 1969 Federal Test Procedure Fuel (3)		1.76	5.88	8.07	3.36
1972 Chevrolet	I	1.52	5.85	7.40	2.72
1972 Federal Test	II	1.44	5.51	7.43	2.56
Procedure	III	1.58	5.79	7.40	2.66
Fuel (5)					
1975 prototype "A"	I	1.46	5.37	7.57	3.01
1972 Federal Test	II	1.04	5.43	8.29	2.78
Procedure	III	1.22	5.14	7.62	3.54
Fuel (5)					
1975 prototype "B"	I	1.37	5.93	7.39	2.72
1972 Federal Test	II	1.02	5.44	7.80	2.87
Procedure	III	1.15	5.49	7.34	2.80
Fuel (5)					

Density HC = density of hydrocarbons in the exhuast gas assuming an average carbon-to-hydrogen ratio of 1:1.85 in grams per cubic foot at 528°R and 760 mm Hg pressure (16.33 g/ft^3).

(Note: Current EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will

result in undue difficulty in clarity. NERC/RTP is providing conversion factors for the particular nonmetric units used in the document: cubic foot = 0.02832 cubic meter.)

HC conc = hydrocarbon concentration of the dilute exhaust sample corrected for background, in ppm carbon equivalent.

The Hydrocarbon Photochemical Reactivity Index combines the reactivity rating with the mass emission of each test phase and weights the test phases appropriately.

$$HPRI = \frac{(0.43 \times Y_{ct} \times R_{ct}) + (0.57 \times Y_{ht} \times R_{ht}) + (Y_s \times R_s)}{7.5} \qquad (7)$$

APPLICATION

As illustrated in Figure 4, in addition to the five nonreactive hydrocarbons, definition of ethylene and propylene is obtained from the chromatographic system. Although the analysis of these compounds is not used in the scheme described, the compounds are relatively abundant in auto exhaust samples and serve as excellent system check peaks. They allow the operator to ensure that the chromatographic carrier gas system is stable. They also account for a major portion of the difference between the fuel and exhaust olefin average carbon number.

The purpose of the defined scheme is to permit relating the various hydrocarbon emission control systems to the photochemical significance of the hydrocarbons being emitted. To illustrate this application, Federal certification runs were conducted with a variety of vehicles as indicated in Table 4.

Table 4. PHOTOCHEMICAL SIGNIFICANCE OF HYDROCARBON EMISSIONS FROM LIGHT-DUTY MOBILE SOURCES

Vehicle description	Test phase	Reactivity class				R	V mix, ft^3	HC conc., ppm C	Y	HPRI
		I Nonreactive, percent	II Reactive paraffins, percent	III Reactive aromatics, percent	IV Reactive olefins, percent					
1972 Chevrolet	Cold transient	23.9	32.2	20.6	23.4	1.98	2955	157.9	7.62	
	Stabilized	27.4	28.9	18.3	25.3	2.04	5102	52.7	4.39	2.76
	Hot transient	18.3	39.1	21.0	21.6	1.93	2997	87.9	4.79	
1975 prototype "A" with catalyst removed	Cold transient	16.3	39.2	24.3	20.2	1.91	2932	138.7	6.64	
	Stabilized	24.0	40.3	15.2	20.6	1.91	5168	27.4	2.31	2.08
	Hot transient	13.9	53.4	16.7	16.0	1.75	3029	117.3	5.80	
1975 prototype "A" with catalyst in place	Cold transient	6.8	54.4	10.0	28.8	2.27	2964	51.8	2.51	
	Stabilized	40.7	23.6	21.4	14.3	1.55	5123	8.4	0.70	0.88
	Hot transient	14.4	61.0	8.4	16.2	1.77	3012	60.6	2.98	
1975 prototype "B" with catalyst in place	Cold transient	16.4	38.4	22.9	22.2	1.99	2952	86.8	4.18	
	Stabilized	38.1	42.0	8.2	11.7	1.57	5097	9.3	0.77	0.79
	Hot transient	27.0	48.5	11.5	13.0	1.62	2995	24.8	1.21	

Prototype "A" gave a 66 percent improvement in mass emissions relative to the 1972 Chevrolet; prototype "B" showed a 69 percent improvement. Prototype "A" also gave a 12 percent improvement in the net reactivity of the emissions, and prototype "B" showed a 16 percent improvement. As illustrated by the data in Table 4, catalytic emission control systems yield definite mass improvement but also reactivity improvement. The degree of mass and reactivity improvement varies between control systems.

The impact of catalytic control systems on individual hydrocarbons, resultant in the variable reactivity gains, is illustrated in Figure 6. As evidenced, the degree of control of the hydrocarbons is variable with individual hydrocarbons. When the catalytic muffler was placed in the appropriate position in the exhaust stream, the methane level was reduced 13 percent, whereas the acetylene was reduced 92 percent, the ethylene 74 percent, and the propylene 83 percent.

An additional compound that may be observed on the chromatographic system when utilized with vehicles without advanced emission control is propadiene. The compound is baseline-resolved with a retention time of about 11.9 minutes, eluting after propylene.

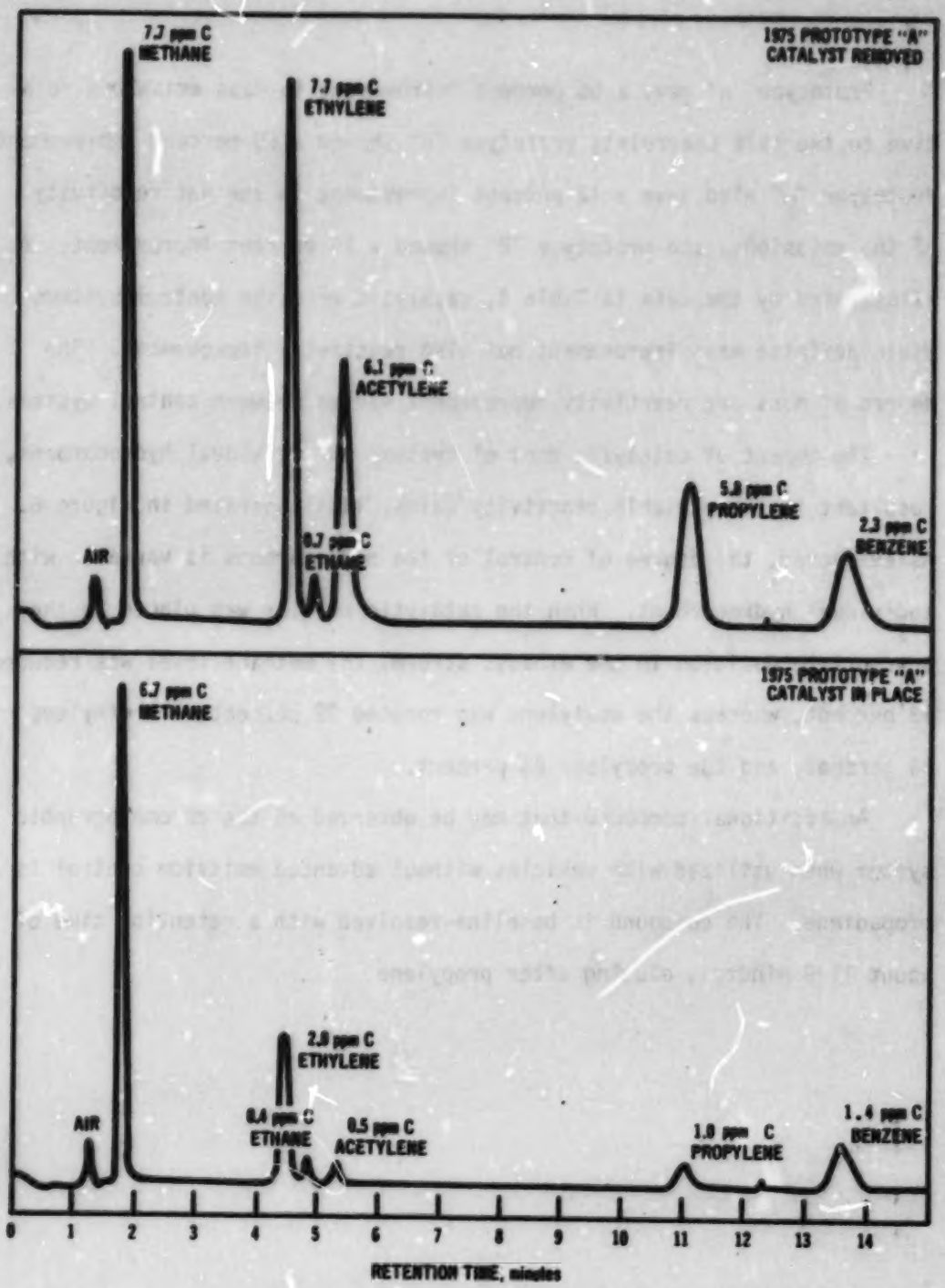

Figure 6. Exhaust chromatogram, catalytic effect.

CONCLUSIONS

The control of hydrocarbon emissions is necessitated by air quality criteria for photochemical oxidants. In view of the fact that hydrocarbons do not participate to the same extent in atmospheric reactions leading to oxidant formation, methods for measurement of more than mass of emissions are necessary to project adequately the impact of mobile sources on photochemical pollution.

Hydrocarbon photochemical reactivity can be integrated with mass measurement methods in varying degrees; total hydrocarbon mass emissions can be measured with no assessment of atmospheric reactivity. Total hydrocarbon less methane levels can be measured, eliminating the most abundant nonreactive hydrocarbons. Total hydrocarbon less methane, ethane, propane, acetylene, and benzene levels can be measured, eliminating the essentially nonreactive hydrocarbons. The emissions can be measured in four hydrocarbon classes, weighting by class reactivity. The emissions can be measured in detail, weighting each individual hydrocarbon by its atmospheric reactivity. Methodology permitting assessment in the first four degrees is available by techniques discussed in this paper. Although only detailed analysis will result in absolute assessment, the procedures described offer a very good approximation of the hydrocarbon photochemical reactivity. The technique is weakened only by the need to estimate class average carbon number. With definition of fuel and vehicle configuration, this estimation can be made relatively accurately.

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